

Barrier to Internal Rotation of Methoxyethyne¹

D. DEN ENGELSEN²

Laboratory of Organic Chemistry, State University, Utrecht

Reinvestigation of the microwave spectrum of methoxyethyne resulted in an accurate value, 1440 ± 30 cal/mole, for the barrier to internal rotation.

In a previous publication (1) of the microwave spectra of methoxyethyne $\text{HC}\equiv\text{COCH}_3$ and the isotopic species $\text{DC}\equiv\text{COCH}_3$ we did not attribute any tilt to the symmetry axis of the methyl group, and it was therefore not possible to calculate a reliable value for the potential barrier hindering the free internal rotation of the CH_3 group. We have now reconsidered these spectra and also assigned several rotational transitions of $\text{HC}\equiv\text{COCH}_3$ to the first excited state of the torsional vibration of the methyl group. In order to fit the barrier parameters satisfactorily to the observed torsion doublets $\nu_A - \nu_E$, it was necessary to abandon the assumption of collinearity of the methyl axis and the O—C (methyl) bond (1). The results of our renewed calculations indicate a tilt of about 5° towards the electron lone pairs of the oxygen atom, see Fig. 1.

EXPERIMENTAL

Microwave absorption spectra were recorded from 17 to 40 GHz with a 10 kHz Stark modulated spectrograph (1). After assigning some extra rotational transitions in the vibrational ground state, it was possible to compute centrifugal distortion constants from the deviations of the rigid rotor frequencies of the rotational transitions (2, 3). Observed and calculated rotational transitions for the vibrational ground state and the first excited torsion vibration of methoxyethyne can be found in Tables Ia and Ib, respectively.

Table II presents the rotational constants, principal moments of inertia and centrifugal distortion parameters. The rotational constants have been modified slightly by taking the centrifugal effect into account (1).

THEORETICAL CONSIDERATIONS

The internal rotation of a molecule with one symmetric internal top is well

¹ Part of a thesis, Utrecht (1968), obtainable upon request.

² Present address: Philips Research Laboratories, N. V. Philips' Gloeilampenfabrieken, Eindhoven, The Netherlands.

TABLE Ia

ROTATIONAL TRANSITIONS OF $\text{HC}\equiv\text{COCH}_3$ IN VIBRATIONAL GROUND STATE (MHz)^a

Transition		Frequency	Delta ^b	Centr. corr.
1 0 1	1 1 0	33274.55	-0.047	-1.771
1 0 1	2 0 2	19571.45	0.055	-0.101
1 1 1	2 1 2	19092.30	-0.038	0.202
1 1 0	2 1 1	20061.95	0.056	0.179
2 0 2	2 1 1	33765.00	0.004	-1.491
2 0 2	3 0 3	29343.65	0.077	-0.341
2 1 2	3 1 3	28635.10	-0.172	0.156
2 2 1	3 2 2	29366.83	-0.005	1.410
2 1 1	3 1 2	30089.30	0.120	0.035
2 2 0	3 2 1	29388.15	0.013	1.401
3 0 3	3 1 2	34510.75	-0.054	-1.115
3 0 3	4 0 4	39099.65	0.096	-0.803
3 1 3	4 1 4	38173.60	-0.111	-0.066
3 1 2	4 1 3	40112.42	0.058	-0.389
3 2 2	4 2 3	39151.20	0.064	1.529
3 2 1	4 2 2	39204.60	-0.027	1.500
3 3 0	4 3 1	39169.22	-0.117	4.429
4 0 4	4 1 3	35523.50	-0.071	-0.701
4 1 4	5 0 5	18158.85	0.088	-1.307
5 0 5	5 1 4	36818.80	0.020	-0.335
5 1 5	6 0 6	28994.40	-0.037	-3.421
6 1 5	5 2 4	35325.90	-0.108	-19.210
6 0 6	6 1 5	38416.00	0.040	-0.135
6 1 6	7 0 7	39979.55	-0.034	-6.265
7 1 7	6 2 4	37830.92	-0.074	-18.672
7 1 6	6 2 5	23893.45	0.178	-14.185
7 0 7	7 1 6	40337.30	0.122	-0.259
8 1 8	7 2 5	30342.60	0.013	-15.435
9 1 9	8 2 6	23263.00	-0.019	-12.121
10 2 9	11 1 10	23961.70	-0.073	-22.037
11 2 10	12 1 11	36416.60	0.073	-36.060

^a Experimental uncertainty about 0.05 MHz; only *A*-components of the torsion doublets have been listed.

^b Observed minus calculated frequency.

understood and has been reviewed thoroughly by Lin and Swalen (4). Following these authors, we can approximate the combination of over-all and internal rotation by an effective Hamiltonian $H_{v\sigma}$ for the *v*th torsional state:

$$H_{v\sigma} = H_{\text{rigid}} + \frac{1}{2rI_\alpha} \sum_n w_{v\sigma}^{(n)} \prod^n \quad (1)$$

in which σ can denote the nondegenerate *A*- or the degenerate *E*-type symmetry

TABLE Ib

ROTATIONAL TRANSITIONS OF $\text{HC}\equiv\text{COCH}_3$, IN THE FIRST EXCITED STATE OF THE TORSION VIBRATION (MHz)^{a, b}

Transition	Frequency	Transition	Frequency		
1 1 1	2 1 2	19057.0	1 0 1	1 1 0	32714.4
1 0 1	2 0 2	19518.0	2 0 2	2 1 1	33187.4
1 1 0	2 1 1	19991.5	3 0 3	3 1 2	33906.6
2 1 2	3 1 3	28588.1	4 0 4	4 1 3	34883.6
2 0 2	3 0 3	29264.5	5 0 5	5 1 4	36133.6
2 1 1	3 1 2	29984.0	6 0 6	6 1 5	37673.3
3 1 3	4 1 4	38101.9	7 0 7	7 1 6	39525.1
3 0 3	4 0 4	38995.8			
3 1 2	4 1 3	39972.9			

^a Experimental uncertainty of the frequencies is about 0.2 MHz.

^b Rotational constants of the *A*-type transitions have been fitted to the above frequencies, taking into account rigid rotor contributions only. The result was: $A_A = 37361.9$; $B_A = 5114.68$; $C_A = C = 4647.48$ MHz. Differences between calculated and measured frequencies nowhere exceed 0.4 MHz.

TABLE II

ROTATIONAL CONSTANTS (MHz), PRINCIPAL MOMENTS OF INERTIA (amu. Å²) AND CENTRIFUGAL DISTORTION CONSTANTS (kHz) OF METHOXYETHYNE (VIBRATIONAL GROUND STATE)^a

<i>A</i> ^b	37928.068 ± 0.04
<i>B</i>	5136.678 ± 0.006
<i>C</i>	4651.795 ± 0.009
<i>I_a</i> ^c	13.3327
<i>I_b</i>	98.419
<i>I_c</i>	108.674
<i>τ_{aaaa}</i>	-7400 ± 35
<i>τ_{bbbb}</i>	-18.8 ± 0.3
<i>τ_{cccc}</i>	-7.3 ± 0.3
<i>τ_{abab}</i>	-72.5 ± 7

^a Compare Ref. (1).

^b Constants for the *A*-components of the torsion doublets.

^c Conversion factor between rotational constants and moments of inertia is 505531 amu. Å². MHz.

state of the torsion vibration of the CH₃ group. Furthermore

$$\prod = I_\alpha \sum_{g=a,b,c} \frac{\lambda_g P_g}{I_g} \quad (2)$$

The symbols *r*, *I_α*, *w_{vσ}⁽ⁿ⁾*, λ_g , *I_g* and *P_g* have their usual meaning (4, 5). For our purpose it was sufficient to consider in eq. (1) terms only up to *n* = 3, even

in the first excited state of the torsion vibration, because higher order terms contribute in this state far less than 1 MHz to the observed doublet splittings $\nu_A - \nu_E$. Hence, the energy matrix of H_{vv} on the basis of eigenfunctions of a symmetric top $|JKM\rangle$ has non-diagonal elements of the type:

$$\langle K | H_{vv} | K \pm 1 \rangle, \quad \langle K | H_{vv} | K \pm 2 \rangle \quad \text{and} \quad \langle K | H_{vv} | K \pm 3 \rangle$$

The direction cosine λ_c of the methyl axis with respect to the c -axis is zero,³ and therefore eq. (2) reduces to:

$$\Pi = I_a \left(\frac{\lambda_a}{I_a} P_a + \frac{\lambda_b}{I_b} P_b \right) \quad (3)$$

Methoxyethyne is a slightly (prolate) asymmetric top molecule (Ray's asymmetry parameter κ being -0.971), which makes a Type I representation ($z \rightarrow a$), defined by King *et al.* (6) practical from a computational point of view. The matrix elements of P_a , P_b (and P_c) on the basis $|JKM\rangle$ are then:

$$\begin{aligned} \langle K | P_a | K \rangle &= \hbar K \\ \langle K \pm 1 | P_b | K \rangle &= \frac{1}{2} \hbar \{ (J \mp K)(J \pm K + 1) \}^{1/2} \\ \langle K \pm 1 | P_c | K \rangle &= -i \langle K \pm 1 | P_b | K \rangle \end{aligned} \quad (4)$$

The phases of the angular momenta in eq. (4) have been chosen so as to avoid complex matrix elements, for P_c does not occur in eq. (3). This particular choice accelerates the computations (matrix diagonalization) considerably. Frequencies of the allowed rotational transitions for the A - and E -type symmetry and their differences $\nu_A - \nu_E$ have been calculated as a function of the moment of inertia of the methyl group I_a about its symmetry axis, the direction cosine λ_a of this axis with respect to the a -axis ($\lambda_b^2 = 1 - \lambda_a^2$) and the barrier height V_3 (the perturbation coefficients $w_{vv}^{(n)}$ are very sensitive to the potential barrier V_3). The frequencies and torsion doublet spacings were computed on the electronic XS computer of the State University of Utrecht.

RESULTS AND DISCUSSIONS

The computations of the doublet spacings indicate that the value of I_a ($3.10 \leq I_a \leq 3.25 \text{ amu} \cdot \text{\AA}^2$) is not very critical for obtaining a satisfactory fit of V_3 . We therefore arbitrarily fixed I_a at $3.15 \text{ amu} \cdot \text{\AA}^2$ (7). A variation of 3% in I_a changes the barrier height V_3 approximately 2%. The direction cosines λ_a and λ_b can be determined fairly accurately from the splittings $\nu_A - \nu_E$ by a method previously described (2). However, since the potential barrier V_3 in

³ C_s or C_{1h} symmetry for $\text{HC}\equiv\text{COCH}_3$ (and $\text{HC}\equiv\text{CSCH}_3$ (2)), is likely enough, because: (a) $I_a + I_b - I_c = I_a - \Delta$; (b) $\mu_c = 0$ (apart from experimental uncertainties (1)); (c) only four centrifugal parameters give a significant contribution to the centrifugal distortion correction of the rotational frequencies (2, 3).

$\text{HC}\equiv\text{COCH}_3$ is lower than in $\text{HC}\equiv\text{CSCH}_3$ the constants ΔA and ΔB (2, 4, 5), which account only for the \prod^2 -term of eq. (1), could not be determined in the oxy-compound from the spectra directly. Exact values of ΔA and ΔB were obtained by correcting the torsion doublets of the rotational transitions in the vibrational ground state for terms linear in the angular momenta, see eq. (1) and eq. (2).

The barrier parameters that give a nice fit are listed in Table III, and Table IV contains the observed and calculated values of the doublet spacings $\nu_A - \nu_B$ of the two assigned rotational spectra. The torsional satellite spectrum distinguishes itself from other satellite spectra and the rotational spectrum in the vibrational ground state by much greater doublet distances $\nu_A - \nu_B$; see Table IV. The small differences between calculated and measured frequency spacing may result from the neglect of higher order terms in the Fourier expansion of the potential barrier (4).

Although the direction of the methyl axis with respect to the principal axes a and b (Table III) is obtained fairly easily from the microwave spectrum of methoxyethyne,⁴ its tilt has to be estimated due to the lack of sufficient structural data. An approximate fit of the structural parameters to the experimental moments of inertia of $\text{HC}\equiv\text{COCH}_3$ and $\text{DC}\equiv\text{COCH}_3$ (1) leads to a value of about 47° for the angle between the O—C (methyl) bond and the a -axis. However, since this latter value is assumed to be correct within 2°, the tilt of the methyl axis (about 5°) is considerable, see Fig. 1.

It might be important from a theoretical point of view to compare several (little known) structural and barrier parameters of several compounds related to methoxyethyne. Table V gives a survey of the interesting quantities for this purpose. All substances in this Table have been investigated by microwave spectroscopy. As can be seen, a general feature of molecules with a nonaxial symmetric distribution of atoms about the axis of the methyl group is a tilt of the latter towards the lone pairs of electrons of oxygen or sulphur. Moreover, the data of Table V suggest a slightly greater tilt in the oxy- than in the corresponding thio-compounds.

The barrier to internal rotation in $\text{HC}\equiv\text{COCH}_3$ is 300 cal/mole lower than that of $\text{HC}\equiv\text{CSCH}_3$ (2). The same situation holds for $\text{N}\equiv\text{CXCH}_3$ (8, 9) and HXCH_3 (10, 11) ($X = \text{O}$ or S) where the molecules containing sulphur possess

⁴ We get two solutions of the equations (2):

$$\lambda_a^2 + \lambda_b^2 = 1$$

and

$$\lambda_a^2/\lambda_b^2 = \frac{\Delta A I_b^2}{\Delta B I_a^2}$$

however, by drawing both possibilities in a molecular model of $\text{HC}\equiv\text{COCH}_3$, one structure can be ruled out.

TABLE III
BARRIER PARAMETERS

I_a	3.15	± 0.1 amu. \AA^2
λ_a	0.74	± 0.005
λ_b	0.67	± 0.005
arc λ_a	42°10'	$\pm 30'$
F	187	± 3 GHz
s	35.95	± 0.2
V_3	1440	± 30 cal/mole

TABLE IV
OBSERVED AND CALCULATED DOUBLET SPACINGS $\nu_A - \nu_B$ (MHz)^a

Transition	Vibr. ground state		First excited torsion vibr.	
	Exp.	Calculated	Exp.	Calculated
1 1 1	2 1 2	-2.85	-2.94	-364.9
1 0 1	2 0 2	+0.47	+0.51	-14.8
1 1 0	2 1 1	+4.17	+3.96	+328.5
2 1 2	3 1 3	—	-0.42	-363.2
2 0 2	3 0 3	+0.80	+0.76	-22.4
2 2 1	3 2 2	-9.47	-9.65	—
2 2 0	3 2 1	+10.58	+11.21	—
2 1 1	3 1 2	+2.05	+1.96	+309.0
3 1 3	4 1 4	—	+0.19	-277.1
3 0 3	4 0 4	+1.00	+1.00	-29.75
3 2 1	4 2 2	+20.70	+20.94	—
3 1 2	4 1 3	—	+1.86	+206.9
1 0 1	1 1 0	+12.15	+12.07	-2151.6
2 0 2	2 1 1	+15.80	+15.51	-1808.1
3 0 3	3 1 2	+17.00	+16.71	-1476.7
4 0 4	4 1 3	+17.60	+17.57	-1241.7
5 0 5	5 1 4	+18.50	+18.41	-1102.4
6 0 6	6 1 5	+19.20	+19.34	-1030.2
7 0 7	7 1 6	+20.10	+20.42	—
4 1 4	5 0 5	-14.80	-14.70	—
5 1 5	6 0 6	-13.60	-13.73	—
6 1 6	7 0 7	-12.18	-12.75	+171.1?
6 1 5	5 2 4	+81.75	+80.24	—
7 1 6	6 2 5	+63.02	+63.69	—

^a See also Ref. (1).

higher potential barriers, whereas CH_3OXH_3 (12) and CH_3SCH_3 (13) show the opposite relation.⁵ We have tried to get an impression of the order of magnitude of the barrier height in $\text{HC}\equiv\text{COCH}_3$ from theoretical arguments. Hoffmann's

⁵ This might be attributed to a stronger steric hindrance of the methyl groups in CH_3OCH_3 .

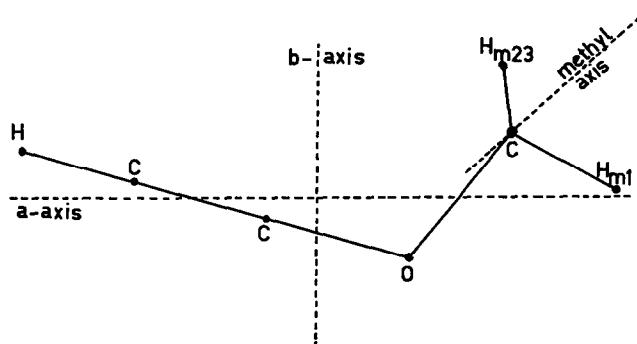
FIG. 1. Molecular model of methoxyethyne; *c*-axis perpendicular to the drawing-plane.

TABLE V
STRUCTURAL DATA (BOND DISTANCES IN \AA UNITS) AND BARRIER HEIGHT (cal/mole) OF
SOME RELATED COMPOUNDS^a

	C—X (short)	C—X (long)	$\angle \text{CXC}$	Tilt	V_b	Ref.
$\text{HC}\equiv\text{COCH}_3$	1.315	1.415 ^b	113°20'	5°	1440	(1)
$\text{N}\equiv\text{COCH}_3$	—	—	—	—	1110	(8)
CH_3OCH_3	—	1.410	111°43'	2°30'	2720	(12)
CH_3OH	—	1.427	—	5°	1070	(10)
CH_3OCl	—	1.389	112°42'	—	3060	(16)
$\text{HC}\equiv\text{CSCH}_3$	1.685	1.813	99°54'	3°	1745	(2)
$\text{N}\equiv\text{CSCH}_3$	1.684	1.820	99°52'	—	1593	(9)
$\text{N}\equiv\text{CSC}\equiv\text{N}$	1.701	—	98°22'	—	—	(17)
CH_3SCH_3	—	1.802	98°52'	2°37'	2132	(13)
CH_3SH	—	1.819	—	2°10'	1270	(11)

^a X stands for O or S.^b Assumed (see also thesis).

"extended Hückel" method (14) was used for computations of this kind.⁶ The staggered conformation appeared to be more stable by an amount of 933 cal/mole, which is in fair agreement with the experimental value, 1440 cal/mole. The "extended Hückel" calculations were based upon the uncertain molecular structure (bond lengths $\pm 0.02 \text{ \AA}$ (1)) as determined from our microwave investigation and the ionization potentials of the following Slater type atomic orbitals:

$$\begin{aligned} 1s(\text{H}) &= 13.6 \text{ eV}; & 2s(\text{C}) &= 21.4 \text{ eV}; & 2p(\text{C}) &= 11.4 \text{ eV}; \\ 2s(\text{O}) &= 35.3 \text{ eV} \quad \text{and} \quad 2p(\text{O}) &= 17.3 \text{ eV}. \end{aligned}$$

Therefore, our computations show the conformation of the methyl group in $\text{HC}\equiv\text{COCH}_3$ (with respect to the acetylenic tail) to be staggered. Reference

⁶ Computer programs by Dr. P. J. A. Ruttink.

should be made to methylthioethyne where a staggered conformation has been derived both from an electron diffraction pattern of $\text{HC}\equiv\text{CSCH}_3$ (15) and the microwave spectrum of $\text{HC}\equiv\text{CSCDH}_2$.⁷

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⁷ Investigated recently by Dr. G. Ruitenberg.